

# Hydrogen absorption and lithium ion conductivity in Li<sub>6</sub>NBr<sub>3</sub>

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## Accepted Manuscript

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Hydrogen absorption and lithium ion conductivity in  $\text{Li}_6\text{NBr}_3$

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## Abstract

The reaction of lithium amide and imide with lithium halides to form new amide halide or imide halide phases has led to improved hydrogen desorption and absorption properties and, for the amides, lithium ion conductivities. Here we investigate the effect of bromide incorporation on the ionic conductivity and hydrogen absorption properties of lithium nitride. For the first time we show that it is possible for a lithium halide nitride, the cubic bromide nitride  $\text{Li}_6\text{NBr}_3$ , to take up hydrogen—a necessary condition for potential use as a reversible solid-state hydrogen storage material. Powder X-ray diffraction showed the formation of  $\text{Li}_2\text{Br}(\text{NH}_2)$  and  $\text{LiBr}$ , and Raman spectroscopy confirmed that only amide anions were present and that the hydrogen uptake reaction had gone to completion. The lithium ion conductivity of  $\text{Li}_6\text{NBr}_3$  at the hydrogenation temperature was found to be less than that of  $\text{Li}_3\text{N}$ , which may be a significant factor in the kinetics of the hydrogenation process.

**Keywords:** hydrogen storage materials, lithium nitride, lithium bromide, lithium ion conductivity, powder X-ray diffraction, A.C. impedance spectroscopy

## 1. Introduction

The ability of many metals and alloys to absorb and store hydrogen has been known for many years [1], but the gravimetric hydrogen densities achieved are too low for many commercial applications. This has resulted in increased research into complex metal hydrides [2, 3]; however, even when these systems exhibit favourable thermodynamic properties for reversible hydrogen desorption, the kinetics of hydrogen desorption and/or absorption remain problematic.

Thermal decomposition of lithium amide ( $\text{LiNH}_2$ ) produces ammonia ( $\text{NH}_3$ ) rather than  $\text{H}_2$ , but the addition of lithium hydride ( $\text{LiH}$ ) creates a pathway that can produce up to 10.3 wt% of hydrogen in two stages (Equation 1) [4, 5], though only the first stage (~6.5 wt%) has been regarded as useful for the reversible storage of hydrogen under practical conditions. Replacing  $\text{LiNH}_2$  with magnesium

amide ( $\text{Mg}(\text{NH}_2)_2$ ), which decomposes at a lower temperature than  $\text{LiNH}_2$ , results in a lower temperature of  $\text{H}_2$  release [6].



More recent work has seen the incorporation of halides into  $\text{LiNH}_2$  and lithium imide ( $\text{Li}_2\text{NH}$ ), which also resulted in the release of  $\text{H}_2$  at lower temperature than  $\text{LiNH}_2$ . Moreover, the resulting lithium imide halides required a lower temperature for hydrogen uptake compared to  $\text{Li}_2\text{NH}$  [7]. Interestingly, the most conducting of these, with room temperature ionic conductivities approaching  $10^{-3} \text{ S cm}^{-1}$ , were the quickest to release hydrogen on heating and to hydrogenate, and unwanted release of  $\text{NH}_3$  was suppressed; it was suggested that improved lithium ion conductivity in the amide halide phases could be the reason for these improved hydrogenation properties [1]. The key role of  $\text{NH}_3$  as an intermediate in the reaction between  $\text{LiNH}_2$  and  $\text{LiH}$  was identified early on [8], but Borgschulte *et al.* [9] later showed that below  $250^\circ\text{C}$  the emission rate of  $\text{NH}_3$  is sufficiently small that reversible dehydrogenation *via* a solid-state reaction may occur [10], controlled by the diffusion of ionic species such as  $\text{Li}^+$  to or from  $\text{LiH}$ .

In comparison, the second stage of the dehydrogenation reaction has attracted comparatively little attention [11–13] as the relatively large reaction enthalpy results in a high temperature of desorption and the kinetics of the reverse reaction are slow. As part of our programme investigating the effect of halides on the ionic conductivity and hydrogen storage properties of lithium nitride ( $\text{Li}_3\text{N}$ ), in this work we report results for the lithium bromide nitride phase  $\text{Li}_6\text{NBr}_3$ .

$\text{Li}_6\text{NBr}_3$  was first synthesized by Sattlegger and Hahn [14] in 1971, who reported an *fcc* structure with Li atoms being ordered in octahedra around the N atoms. This material was examined as a potential lithium ion conductor by Hartwig *et al.* [15]. Over 25 years after the original structural characterization by Sattlegger, Marx and Ibberson [16] used powder neutron diffraction to determine the Li distribution more accurately, but were unable to distinguish between two different possibilities: the first where the Li are disordered over distorted tetrahedral, and the second where they are disordered around the N atom in an octahedral configuration. Marx [17], and Marx and Ibberson [16],

also studied phase changes that occurred at elevated and cryogenic temperatures. Here we report for the first time the hydrogenation of a lithium nitride halide and compare its hydrogen uptake properties to those of  $\text{Li}_3\text{N}$ .

## 2. Experimental

Lithium bromide nitride ( $\text{Li}_6\text{NBr}_3$ ) was synthesized through direct solid state reaction of stoichiometric amounts of  $\text{Li}_3\text{N}$  (Sigma–Aldrich, 99.5% purity) and  $\text{LiBr}$  (Sigma–Aldrich, 99.999% purity), which were ground together in an agate pestle and mortar to achieve a homogeneous mixture. The ground powder was then transferred into a quartz tube lined with a metal (vanadium or nickel) sleeve. These manipulations were performed in an argon-filled glovebox to avoid contact with the atmosphere. The tube was evacuated under high vacuum, and sealed using an oxygen gas torch. The sealed tube was then heated at  $430^\circ\text{C}$  for 24 h followed by cooling down to ambient temperature, with heating and cooling rates of  $50^\circ\text{C}/\text{h}$ . Hydrogenations were performed for 24 hours in a high pressure hydrogenator under 90 bar  $\text{H}_2$  at temperatures between  $150$ – $250^\circ\text{C}$ . As a comparison  $\text{Li}_3\text{N}$  was hydrogenated under similar conditions.

For phase characterization, all powders were reground and packed into polyimide capillary tubes, which were sealed with an airtight adhesive. Powder X-ray diffraction (XRD) data were collected in the  $2\theta$  range  $10$ – $90^\circ$  in capillary transmission geometry on a Siemens D5000 diffractometer with a  $\text{CuK}_{\alpha 1}$  radiation source and position sensitive detector. The data were analysed using the TOPAS refinement suite [18].

For A.C. impedance spectroscopy measurements,  $\text{Li}_6\text{NBr}_3$  powder was pressed into pellets under a load of 1 ton. The pressed pellets were sintered at  $400^\circ\text{C}$  for 3 h in evacuated quartz tubes, and the sintered pellets were then coated with silver to ensure good electrical contact at the surfaces and silver foil electrodes affixed. Typical sintered pellets were 6.9 mm in diameter, 1.0 mm thick with density  $\sim 83\%$  of theoretical. A.C. impedance measurements were carried out under an argon atmosphere on a N4L PSM1735 phase-sensitive multimeter with impedance analysis interface. Equivalent circuits were used to calculate the resistance from the Nyquist plots. The impedance data showed a single

semicircle at the lowest temperature, with an additional spike seen at higher temperatures associated with the electrode response. For the semicircle, a single parallel circuit of  $R||CPE$  was used as a model, indicating that it was not possible to resolve bulk and grain boundary components, and so the conductivities reported represent total conductivities.

Raman spectra were collected on a Renishaw inVia Raman microscope operating with a 633nm excitation laser. Samples were sealed inside airtight containers under an argon atmosphere.

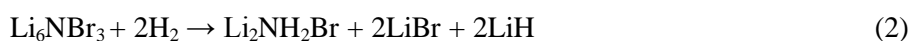
### 3. Results and discussion

#### 3.1 Synthesis of $Li_6NBr_3$

$Li_6NBr_3$  was synthesized as described above. A limited Rietveld refinement, where only unit cell parameters were refined, was carried out against powder XRD data obtained from the product using the structural model reported by Marx and Ibberson [16] (space group  $Fm\bar{3}m$ ); experimental, calculated and difference profiles are shown in Figure 1. The lattice parameter refined to  $a = 8.9334(1)$  Å, comparable to that previously reported of  $a = 8.93896(4)$  Å.

#### 3.2 Hydrogenation of $Li_6NBr_3$ and $Li_3N$

Hydrogenation of  $Li_6NBr_3$  was attempted for 24 hours at temperatures between 150–250°C under 90 bar  $H_2$ . It was found that no hydrogenation occurred at temperatures lower than 250°C. At 250°C, the compound was found to hydrogenate to give  $Li_2NH_2Br$  and  $LiBr$ . It is expected that  $LiH$  was also produced in the hydrogenation reaction (see Equation 2), but this compound is often difficult to observe in powder XRD patterns owing to the low scattering factors of Li and H. Rietveld refinement of the unit cell parameters using the structural model of  $Li_2NH_2Br$  as reported by Barlage and Jacobs [19] (space group  $Pnma$ ), and the rock salt structure for  $LiBr$ , resulted in values of  $a = 12.4882(4)$  Å,  $b = 8.0090(2)$  Å,  $c = 6.3710(2)$  Å, which are comparable to those previously reported [19] for  $Li_2NH_2Br$ ,  $a = 12.484(2)$  Å,  $b = 7.959(1)$  Å,  $c = 6.385(1)$  Å. Experimental, calculated and difference profiles are shown in Figure 2a.



As it is possible that not all the products of hydrogenation were crystalline, Raman spectroscopy was used to examine if the hydrogenation reaction was complete. The Raman spectrum of the hydrogenated products (Figure 2b) shows at least three peaks at  $\sim 3220$ ,  $3245$  and  $3280\text{ cm}^{-1}$ . All of these are higher in frequency than imide stretching vibrations we have observed in lithium imide and a range of lithium imide halides ( $< 2200\text{ cm}^{-1}$ ) and are consistent with  $\text{NH}_2^-$  stretching modes and the observation of the amide  $\text{Li}_2\text{NH}_2\text{Br}$  as the main hydrogenation product in the powder XRD pattern. The broadness of the peaks observed between  $3200\text{--}3250\text{ cm}^{-1}$  may be indicative of some disorder within the  $\text{Li}_2\text{NH}_2\text{Br}$  structure or possibly the presence of a secondary amorphous phase.

As a comparison  $\text{Li}_3\text{N}$  was hydrogenated under the same conditions; it was found that the nitride hydrogenated at lower temperature ( $150^\circ\text{C}$ ) than  $\text{Li}_6\text{NBr}_3$ .

### 3.3 A.C. impedance spectroscopy

The conductivity of  $\text{Li}_6\text{NBr}_3$  was measured from  $65\text{--}310^\circ\text{C}$ . The Nyquist plot showed a single semicircle at high frequency (Figure 3a) assigned to total conductivity. The conductivity was calculated to be  $\sigma_{(65^\circ\text{C})} = 1.86 \times 10^{-7}\text{ S cm}^{-1}$ , which is comparable to previous reports [15]. A temperature-dependent plot of the conductivity of  $\text{Li}_6\text{NBr}_3$  is shown in Figure 3b; the activation energy was calculated from the line of best fit for data below  $197^\circ\text{C}$  to be  $0.69(2)\text{ eV}$ .  $\text{Li}_3\text{N}$  ionic conductivity was also measured as a comparison: at  $250^\circ\text{C}$  it was found to be  $\sigma_{(250^\circ\text{C})} = 2.0 \times 10^{-2}\text{ S cm}^{-1}$ , which is more than 10 times higher than  $\text{Li}_6\text{NBr}_3$  ( $\sigma_{(250^\circ\text{C})} \approx 10^{-3}\text{ S cm}^{-1}$ ).

It is interesting that  $\text{Li}_6\text{NBr}_3$  was harder to hydrogenate under the conditions of our experiments than  $\text{Li}_3\text{N}$ . Thermodynamic data are not yet available for the bromide-containing phases, so a thermodynamic explanation for this cannot be discounted, but as the hydrogenated product is thermodynamically favoured at low temperatures in reversible systems, hydrogenation is in practice often kinetically limited. Hydrogen adsorption by  $\text{Li}_3\text{N}$  is strongly exothermic, so the observation that the absorption is thermally activated can only be explained by slow kinetics. It follows that these observations are consistent with the lower ionic conductivity of  $\text{Li}_6\text{NBr}_3$  and the proposal that this is an important parameter in the kinetics of rehydrogenation [7, 9, 10].



The  $\text{Li}_3\text{N}$  structure consists of planar hexagonal layers of lithium cations each centred by a nitride anion. Each  $\text{Li}_6\text{N}$  hexagon is capped above and below the  $ab$  plane by further  $\text{Li}^+$  ions to form a linear  $\text{Li}_2\text{N}$  coordination [20]. The structure of  $\text{Li}_6\text{NBr}_3$  can be understood as a *ccp* arrangement of the  $\text{Br}^-$  ions at the 4a site, with the  $\text{N}^{3-}$  ions at 4b filling all of the octahedral holes and further  $\text{Br}^-$  ions at 8c filling all the tetrahedral holes, which clearly limits the amount of available space in the structure. Six lithium ions are located around  $\text{N}^{3-}$  to form an octahedron. For bulk lithium transport  $\text{Li}$  cations have to move from one nitride ion to a neighbouring one and must pass through a coordination environment, in which it would be coordinated to 4  $\text{Br}^-$  ions only. This is likely to increase the energy of diffusion, thus explaining why the conductivity is lower in the  $\text{Li}_6\text{NBr}_3$  system compared to  $\text{Li}_3\text{N}$ . A comparison of the structures of  $\text{Li}_6\text{NBr}_3$ , indicating the proposed diffusion pathway, and  $\text{Li}_3\text{N}$  is given in Figure 4.

#### 4. Conclusion

$\text{Li}_6\text{NBr}_3$  was successfully synthesized through direct solid state reaction of  $\text{Li}_3\text{N}$  and  $\text{LiBr}$ . Powder XRD showed a diffraction pattern that matched previous reports with comparable lattice parameter and space group  $Fm\bar{3}m$ .

Powder XRD studies showed that  $\text{Li}_6\text{NBr}_3$  can be hydrogenated at  $250^\circ\text{C}$  under 90 bar  $\text{H}_2$  to give  $\text{Li}_2\text{Br}(\text{NH}_2)$  and  $\text{LiBr}$ ; Raman spectroscopy confirmed that only amide anions were present and that the hydrogenation had gone to completion. Under similar conditions it was found that hydrogenation of  $\text{Li}_3\text{N}$  occurred at significantly lower temperature than that of  $\text{Li}_6\text{NBr}_3$ . This observation is consistent with the lower ionic conductivity of  $\text{Li}_6\text{NBr}_3$ , as determined by A.C. impedance spectroscopy, and the proposal that this is an important parameter in the kinetics of rehydrogenation.

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## Figure List

**Figure 1.** Observed, calculated and difference Rietveld powder XRD profiles for  $\text{Li}_6\text{NBr}_3$ .

**Figure 2.** a) Observed, calculated and difference Rietveld powder XRD profiles for hydrogenated  $\text{Li}_6\text{NBr}_3$  at 250°C under 90 bar  $\text{H}_2$  (upper tick marks  $\text{LiBr}$ , lower tick marks  $\text{Li}_2\text{BrNH}_2$ ) ; b) Raman spectrum of hydrogenated  $\text{Li}_6\text{NBr}_3$ .

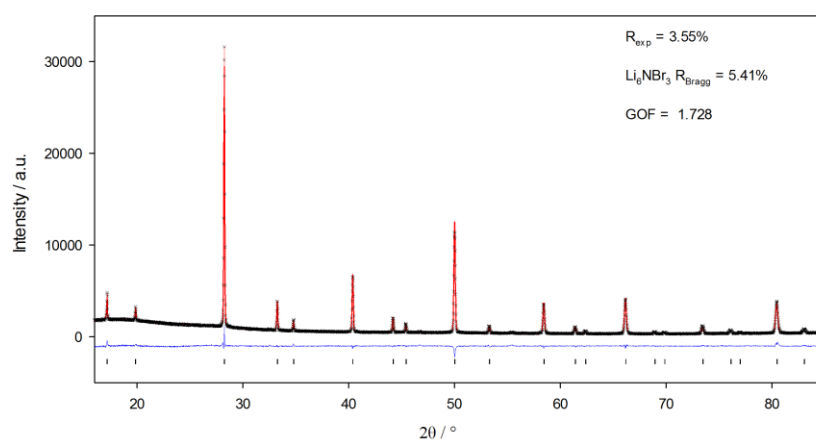
**Figure 3.** a) Experimental (circles) and calculated (dashed line) Nyquist plot for  $\text{Li}_6\text{NBr}_3$  at 197°C; b) Arrhenius plot for  $\text{Li}_6\text{NBr}_3$  from 65–310°C.

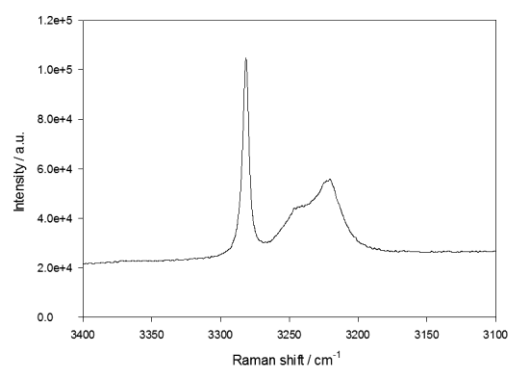
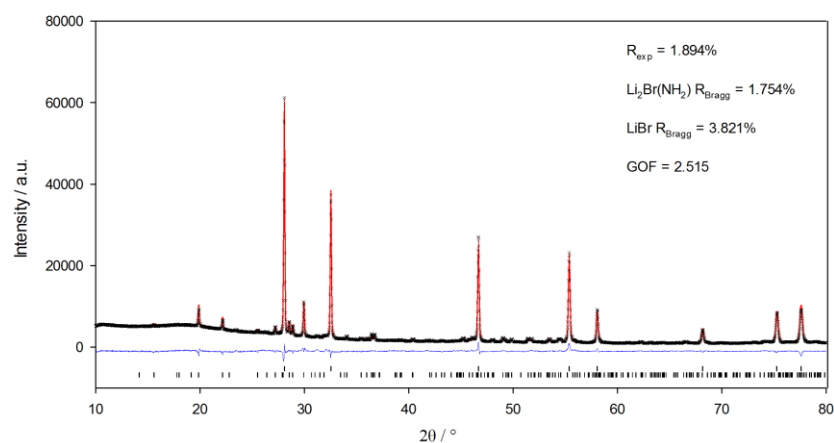
**Figure 4.** Structures of a)  $\text{Li}_3\text{NBr}_3$ , with proposed pathway for lithium ion diffusion indicated by an arrow, and b)  $\text{Li}_3\text{N}$ .

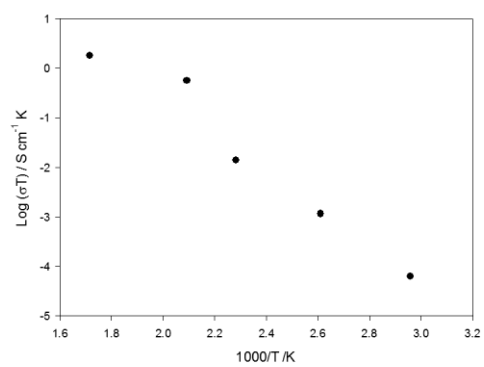
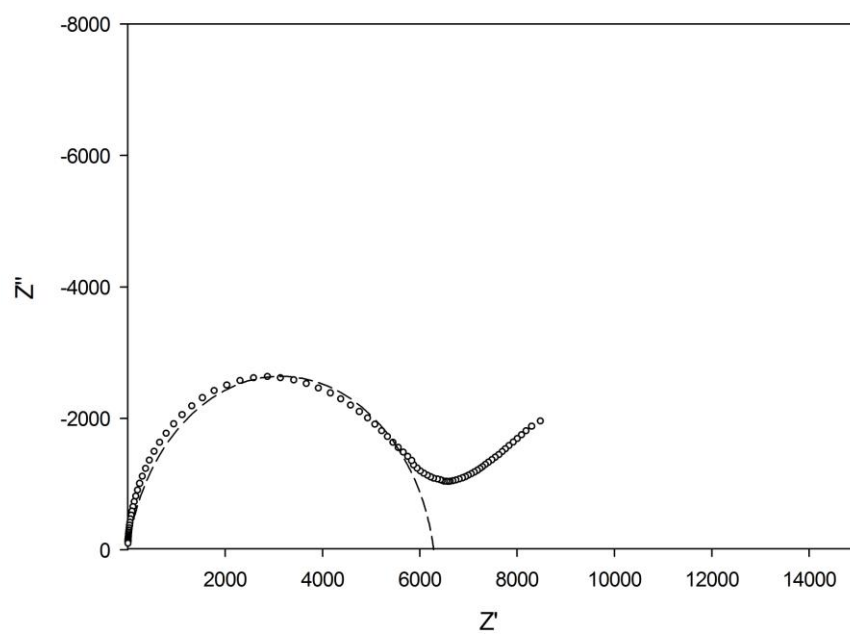
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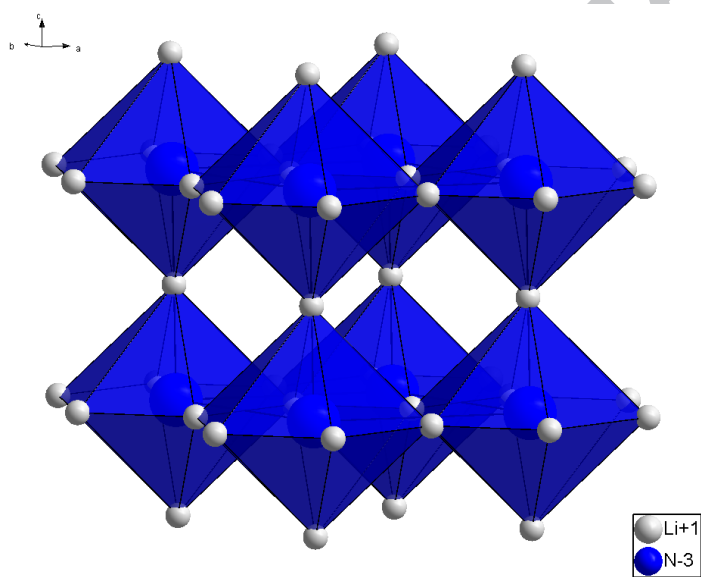
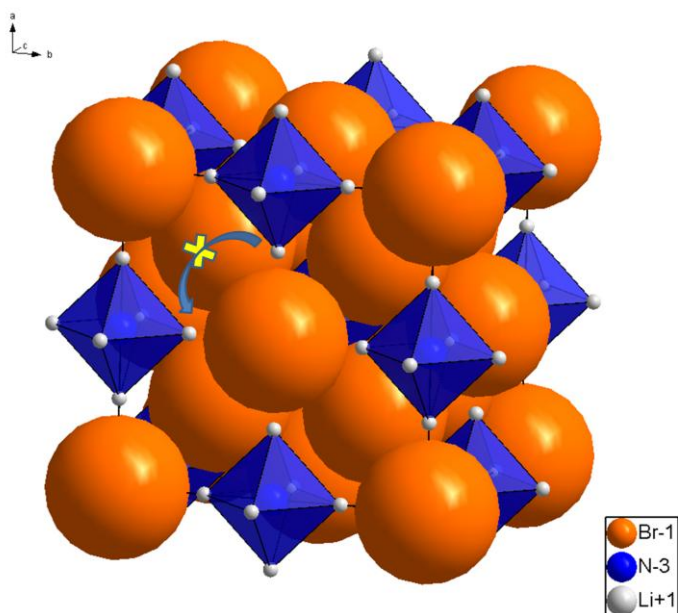
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**Highlights**

- $\text{Li}_6\text{NBr}_3$  was synthesized *via* solid state methods and hydrogenation attempted.
- Hydrogenation of a lithium nitride halide was demonstrated for the first time.
- Powder XRD and Raman spectroscopy showed that hydrogenation had gone to completion.
- The ionic conductivities of  $\text{Li}_6\text{NBr}_3$  and  $\text{Li}_3\text{N}$  were compared through A. C. impedance spectroscopy.
- The lower conductivity of  $\text{Li}_6\text{NBr}_3$  is consistent with its higher hydrogenation temperature.